JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © *Copyright, 1969, by the American Chemical Society*

VOLUME 91, NUMBER 16 JULY 30, 1969

Physical and Inorganic Chemistry

Lifetimes of Amine–Water and Amine–Alcohol Hydrogen-Bonded Complexes in Hydroxylic Solvents. Role of London Dispersion Forces in Solvation[1]

Ernest Grunwald, Robert L. Lipnick, and Earle K. Ralph

Contribution from the Chemistry Department, Brandeis University, Waltham, Massachusetts 02154.

Received November 23, 1968

Abstract: The effect of nonpolar groups on the rate constant k_H for dissociation of amine–hydrate and amine–alcoholate hydrogen-bonded complexes was studied using N,N-diethyl-*m*-toluidine (B) as substrate and methanol and 11.47 mole % *t*-BuOH–88.53 mole % HOH as solvents. k_H was obtained by kinetic analysis of rates of proton exchange, measured by the nmr technique, between BH^+ and OH protons in the solvent. For $B \cdot HOCH_3$ in methanol, $k_H = 4.3 \times 10^8$ sec^{-1} at 30°. For $B \cdot HOH$ and $B \cdot HOBu$-*t* in 11.47% *t*-BuOH–water, $k_H = 6.6 \times 10^9$ and 2.6×10^5 sec^{-1}, respectively, at 25°. The very large effect of alkyl substitution in the hydroxylic molecule on k_H can be attributed largely to London dispersion interaction involving the nonpolar groups.

It is clear from kinetic studies of proton exchange that the dissociation of an ammonium ion as a Brønsted acid in water must be formulated as shown in eq 1.[2,3]

$$\text{Amine H}^+ \cdot OH_2 + H_2O \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{Amine} \cdot HOH + H_3O^+ \quad (1)$$

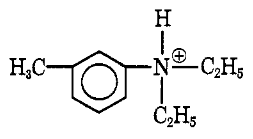
The proton of the original N–H bond remains hydrogen-bonded to the nitrogen atom in the amine hydrate that is formed. If the hydrate reacts with hydronium ion before its water molecule is replaced by a water molecule from the bulk solvent (eq 2), Amine $H^+ \cdot OH_2$ is

$$\text{Amine} \cdot HOH + H_2O(aq) \xrightarrow{k_H} \text{Amine} \cdot HOH + HOH(aq) \quad (2)$$

regenerated without proton exchange. The rate law characteristic of that mechanism is given in eq 3, which is consistent with observation.[2]

$$\text{rate of proton exchange} = k_a k_H[\text{Amine H}^+]/(k_H + k_{-a}[H^+]) \quad (3)$$

We now wish to report a study of NH-proton exchange of N,N-diethyl-*m*-toluidinium ion (BH^+) in methanol and in the two-component solvent, 11.47 mole % *t*-butyl alcohol–88.53 mole % water. BH^+ is



BH^+

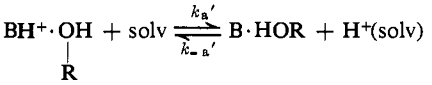
one of the few tertiary ammonium ions with fairly large nonpolar groups attached to nitrogen whose solubility and acid strength are such as to permit precise measurement of proton exchange rates by the nmr method. We find that in methanol, proton exchange resulting from acid dissociation follows the same kinetics (eq 3) as in water. On the other hand, in the *t*-butyl alcohol–water solvent, proton exchange resulting from acid dissociation gives rise to two kinetic terms, each of the mathematical form of eq 3, but with distinctly different values for the rate constants. We interpret this observation as resulting from parallel reactions, one involving the hydrate of BH^+ and the other the alcoholate. In eq 4 and 5, we are using R to

---

(1) Work supported in part by the National Science Foundation and by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to that foundation and to the donors of that fund.

(2) E. Grunwald and E. K. Ralph, *J. Am. Chem. Soc.*, **89**, 4405 (1967), and references cited therein.

(3) M. Cocivera, *J. Phys. Chem.*, 72, 2515, 2520 (1968).



$$\underset{\substack{|\\ \mathrm{R}}}{\mathrm{BH^+\cdot OH}} + \mathrm{solv} \underset{k_{-a}'}{\overset{k_a'}{\rightleftharpoons}} \mathrm{B\cdot HOR} + \mathrm{H^+(solv)} \qquad (4a)$$

$$\mathrm{B\cdot HOR} + \mathrm{solv} \xrightarrow{k_H'} \mathrm{B\cdot solv} + \mathrm{ROH} \qquad (4b)$$

$$\mathrm{BH^+\cdot OH_2} + \mathrm{solv} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \mathrm{B\cdot HOH} + \mathrm{H^+(solv)} \qquad (5a)$$

$$\mathrm{B\cdot HOH} + \mathrm{solv} \xrightarrow{k_H} \mathrm{B\cdot solv} + \mathrm{HOH} \qquad (5b)$$

denote *t*-butyl, primed symbols to denote rate constants for the alcoholate, and unprimed symbols to denote rate constants for the hydrate.

The rate constants k_H and k_H' obtained in this way are very different. k_H is of the same order of magnitude as rate constants for dissociation of amine hydrates in water. k_H' is smaller than k_H by about *four orders of magnitude!* In methanol, where we find only one dissociation process, k_H is intermediate.

Our results are most instructive concerning the solvation of solutes in hydroxylic solvents. Theoretical analysis of solvation must allow for solute–solvent interaction, solvent–solvent interaction, and the modification of one by the other. When *t*-butyl alcohol is added to water, many solvent properties change drastically and in such a way as to suggest that the interaction among the hydroxylic molecules becomes quite different from that among water molecules in pure water.[4] Our measurements of the rate constant, k_H, for the dissociation of specific solvates enable us to decide to what extent the change in solvent–solvent interaction affects the stability of the solute: we find that the solvent–solvent interaction is relatively less important than the solvent–solute interaction. Indeed, our present data on the interaction of a nonpolar amine with three different hydroxylic solvent species (HOH, CH_3OH, and *t*-BuOH) in two different solvents, and our previous data[2] on the interaction of a series of amines with H_2O in water, can be readily accommodated by a single theory in which the solute–solvent interaction dominates. In that theory, the interaction of the hydrophobic parts of the solute and solvent molecules is predictable fairly accurately from London dispersion forces.[5]

Kinetic Part

Proton Exchange in *t*-BuOH–HOH. We found two reactions that contribute to NH-proton exchange: acid dissociation (eq 4 and 5) and symmetrical proton exchange involving BH^+, solvent, and B (eq 6). The

$$\mathrm{BH^+} + \mathrm{solv(OH)} + \mathrm{B} \xrightarrow{k_2} \mathrm{B} + \mathrm{(HO)solv} + \mathrm{HB^+} \qquad (6)$$

total rate of exchange, R, thus consisted of two additive contributions (eq 7).

$$R = R_{\text{acid diss}} + k_2[\mathrm{BH^+}][\mathrm{B}] \qquad (7)$$

To derive an expression for $R_{\text{acid diss}}$, we shall assume that the formal species BH^+ consists of two subspecies, $BH^+\cdot OH_2$ (fraction α) and $BH^+\cdot(OH)R$ (fraction $1 - \alpha$). We shall assume, further, that the products of acid dissociation are B·HOH and B·HOR, as shown in (5a) and (4a). Therefore $R_{\text{acid diss}}$ is equal to $k_H[\mathrm{B\cdot HOH}] + k_H'[\mathrm{B\cdot HOR}]$. On solving for the steady-state concentrations of these solvated bases, we obtain the rate law (8). The two kinetic terms in (8) can be

$$R_{\text{acid diss}} = \frac{\alpha k_a k_H[\mathrm{BH^+}]}{k_H + k_{-a}[\mathrm{H^+}]} + \frac{(1 - \alpha)k_a' k_H'[\mathrm{BH^+}]}{k_H' + k_{-a}'[\mathrm{H^+}]} \qquad (8)$$

resolved experimentally if αk_a is comparable in magnitude to $(1 - \alpha)k_a'$, and if k_{-a}/k_H is very different from k_{-a}'/k_H'. Previous measurements in this solvent[6] for the substrate, imidazolium ion, failed to resolve the two terms, presumably because one or both of these conditions failed to be satisfied.

Equation 8 may be simplified further to permit direct evaluation of k_H and k_H', as follows. Rate constants for reaction of the solvated hydrogen ion with solvated amines are very high and quite nonspecific,[2,3,6-8] suggesting that these processes are diffusion controlled. There is little steric hindrance,[3,9] and the relative mobility of the reactants is approximately equal to the mobility of the hydrogen ion, which is high compared to that of the amine. Therefore, to an approximation well within a factor of 2, we may equate k_{-a} and k_{-a}' to their mean value, $\langle k_{-a}\rangle$. Then for the formal process of acid dissociation, dynamic equilibrium is expressed by (9a) and thermodynamic equilibrium by (9b). Finally, from (7) to (9) we obtain the approximate

$$[\alpha k_a + (1 - \alpha)k_a'][\mathrm{BH^+}] = \langle k_{-a}\rangle[\mathrm{B}][\mathrm{H^+}] \qquad (9a)$$

$$K_A = [\mathrm{B}][\mathrm{H^+}]/[\mathrm{BH^+}] \qquad (9b)$$

working equations

$$\frac{R}{[\mathrm{BH^+}]} = \frac{\alpha k_a}{1 + \langle k_{-a}\rangle[\mathrm{H^+}]/k_H} + \frac{(1 - \alpha)k_a'}{1 + \langle k_{-a}\rangle[\mathrm{H^+}]/k_H'} + k_2[\mathrm{B}] \qquad (10a)$$

$$\langle k_{-a}\rangle = [\alpha k_a + (1 - \alpha)k_a']/K_A \qquad (10b)$$

The rate law (10a) involves five unknown parameters: αk_a, $(1 - \alpha)k_a'$, k_H, k_H', and k_2. $\langle k_{-a}\rangle$ is known through (10b). To secure the rate law we did more than 80 experiments, in which the hydrogen ion concentration ranged from 3.6×10^{-5} to 2.6 *M* and the BH^+ concentration ranged from 0.1 to 0.35 *M*. The first two terms on the right in (10a) depend on $[H^+]$; the third term depends on [B]. To evaluate k_2 we did two series of experiments in which [B] was varied at constant pH. The results are shown in Figure 1. The slopes, which measure k_2, are independent of pH within the experimental error. The intercepts depend on pH, in accordance with (10a).

The remaining parameters in eq 10a were determined by careful analysis of $R/[\mathrm{BH^+}] - k_2[\mathrm{B}]$ as a function of pH. The data are plotted in Figure 2. Although there is scatter consistent with a precision of about 10%, the plot clearly establishes certain features of the functional relationship. Data for 0.2 *M* and 0.1 *M* $[BH^+]$ are scattered about the same average curve; that is, the kinetics is first-order in $[BH^+]$. There are two

---

(4) (a) F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966); (b) M. J. Blandamer, J. A. Buvati, M. F. Fox, M. C. R. Symons, and G. S. P. Verma, *Trans. Faraday Soc.*, **63**, 1850 (1967); (c) M. J. Blandamer, M. C. R. Symons, and M. J. Wooten, *ibid.*, **63**, 2337 (1967); (d) M. J. Blandamer, D. E. Clarke, N. J. Hidden, and M. C. R. Symons, *ibid.*, **64**, 2691 (1968).

(5) F. London, *J. Phys. Chem.*, **46**, 305 (1942).

(6) E. K. Ralph and E. Grunwald, *J. Am. Chem. Soc.*, **91**, 2429 (1969).

(7) E. Grunwald, *J. Phys. Chem.*, **71**, 1846 (1967).

(8) M. Sheinblatt and H. S. Gutowsky, *J. Am. Chem. Soc.*, **86**, 4814 (1964).

(9) E. K. Ralph and E. Grunwald, *ibid.*, **89**, 2963 (1967).

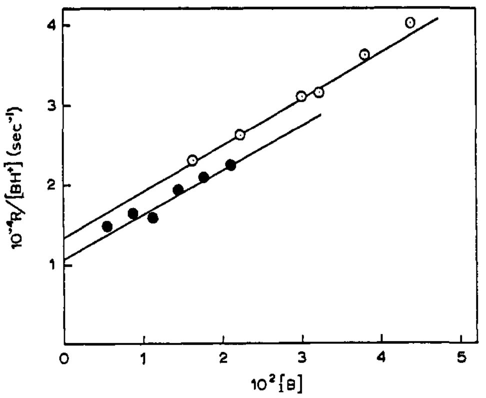


Figure 1. Proton-exchange kinetics of N,N-diethyl-*m*-toluidinium ion (BH^+) in 11.47 mole % *t*-BuOH–88.53 mole % water at 25°: open circles, pH is constant at 4.45; solid circles, pH is constant at 4.15. The straight lines correspond to $k_2 = 6.0 \times 10^5$ sec^{-1} M^{-1}.

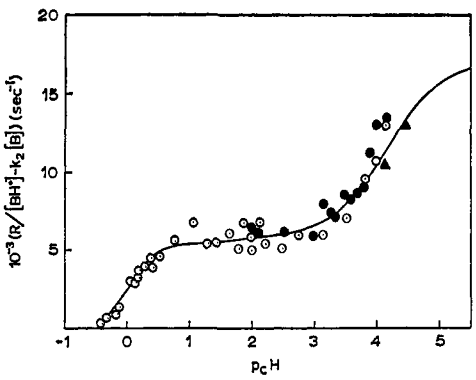


Figure 2. Representative data to show the proton-exchange kinetics of N,N-diethyl-*m*-toluidinium ion (BH^+) in 11.47 mole % *t*-BuOH–88.53 mole % water at 25°: open circles, $[BH^+] = 0.2\ M$; solid circles, $[BH^+] = 0.1\ M$; triangles, $[BH^+] = 0.0\ M$ (intercepts of Figure 1). The smooth curve is a plot of eq 10a, using rate constants as listed in Table I.

regions of pH in which the ordinate in Figure 2 is changing, and a rather wide intermediate region in which it is constant. In terms of eq 10a, in the region of constant ordinate $\langle k_{-a}\rangle[H^+]/k_H \ll 1$, $\langle k_{-a}\rangle[H^+]/k_H' \gg 1$, and the constant value of the ordinate is equal to αk_a, which is thereby determined accurately.

The region of low pH, in which the ordinate decreases towards zero, may be analyzed to give $\langle k_{-a}\rangle/k_H$ with an accuracy of better than 20%, and hence k_H. The region of high pH, in which the ordinate increases above the constant value αk_a, may be analyzed to give $(1 - \alpha)k_a'$ and $\langle k_{-a}\rangle/k_H'$, and hence k_H'. It was not possible to extend measurements to such a high pH that the ordinate attain its theoretical maximum value of $[\alpha k_a + (1 - \alpha)k_a']$. However, the data near the highest pH do seem to show the predicted inflection point. If this be granted, then $(1 - \alpha)k_a'$ and k_H' are determined with an accuracy of 50% or better. Results of the kinetic analysis, including K_A and $\langle k_{-a}\rangle$, are summarized in Table I.

Table I. Rate Constants for NH-Proton Exchange of N,N-Diethyl-*m*-toluidinium Ion

Measured quantity	*t*-BuOH–HOH at 25°[a]			MeOH at 30°
	B·HOH		B·HOBu-*t*	B·HOMe
$10^{-3}k_a$, sec^{-1}	$5.9/\alpha$		$11.3/(1 - \alpha)$	0.180[b]
$\langle k_{-a}\rangle$, sec^{-1} M^{-1}	3.9×10^9		3.9×10^9	1.3×10^9
k_H, sec^{-1}	6.6×10^9		2.6×10^5	4.3×10^8
Formal pK_A		5.36		6.85[c]
Formal k_2, sec^{-1} M^{-1}		6.0×10^5		4.2×10^5 [d]

[a] 11.47 mole % *t*-BuOH–88.53 mole % water. [b] On the basis of measurements at 11.1, 20.6, 29.8, 39.1, and 48.4°, log $k_a = 9.853 - 2290/T$; $E_{act} = 10.48 \pm 0.39$ kcal; correlation coefficient = 0.994. [c] From slow-passage line-shape measurements of the CH_3-proton resonance of methanol near pH 8, as described in ref 18. Potentiometric value at 22°, pK_A = 6.94. [d] From slow-passage line-shape measurements of the CH_3-proton resonance of methanol[16] near pH 8, $k_2 = (3.9 \pm 0.4) \times 10^5$ sec^{-1} M^{-1}. Thus the number of methanol molecules participating in reaction 6 is $(3.9 \pm 0.4)/4.2$, or one molecule.

Proton Exchange in Methanol. Nmr methods for measuring rates of NH–OH proton exchange in methanol and the number of methanol molecules that participate in the kinetic processes have been described previously.[10] Our data for BH^+ in methanol are represented satisfactorily by the rate law

$$\frac{R}{[BH^+]} = \frac{k_a k_H}{k_H + k_{-a}[H^+]} + k_2[B] \qquad (11)$$

To establish this rate law, we did more than 50 experiments in which the hydrogen ion concentration ranged from 3.6×10^{-7} to 1.0 M and the BH^+ concentration ranged from 0.05 to 0.21 M. Relevant data are shown in Figures 3 and 4. In Figure 3 the term $k_2[B]$ becomes significant only above pH ≈3.5; at lower pH we see the kinetics of proton exchange due to acid dissociation. Figure 4 shows a kinetic plot for the region of high pH in which the term $k_2[B]$ dominates.

In the interpretation of proton exchange resulting from acid dissociation in the *t*-butyl alcohol–water solvent, we had assigned the two kinetic terms that are independent of [B] in (10a) to separate reactions of a hydrate and an alcoholate. If that interpretation is correct, then in methanol, where there can be only an alcoholate, there would be only one kinetic term due to acid dissociation that is independent of [B], as claimed in eq 11. On the other hand, if the pH–rate profile observed in *t*-butyl alcohol–water were due to the presence of two slowly interconverting isomeric subspecies of BH^+, or due to some other intrinsic property of BH^+, we would expect to find a similar pH–rate profile in methanol. In order to show that eq 11 is indeed adequate, we have included in Figure 3 the deviations of the experimental points from the curve giving best fit to all the data. Below pH 3.5 the deviations are random. Between pH 3.5 and 5.0 the deviations tend to be negative. They amount to about 10% of $R/[BH^+]$ and are probably still within the experimental error. Above pH 5.0, the deviations are

---

(10) M. Cocivera, E. Grunwald, and C. F. Jumper, *J. Phys. Chem.*, **68**, 3234 (1964).

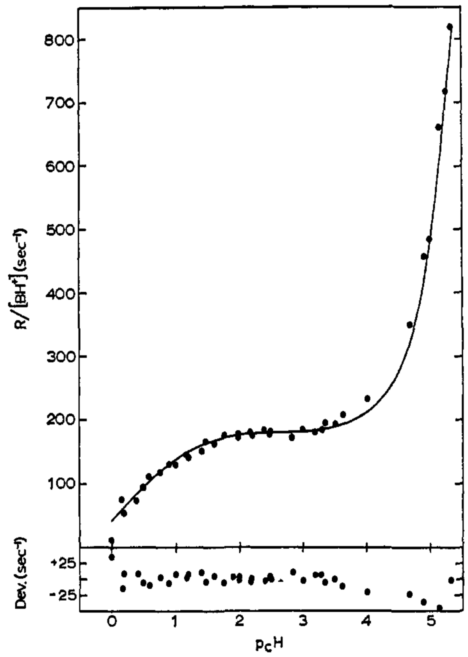


Figure 3. Representative data to show the proton-exchange kinetics of BH^+ in methanol at 30°. Above pH 3.5, $[BH^+]$ is constant at 0.0521 *M*. The smooth curve is a plot of eq 11, using rate constants as listed in Table I. Deviations are defined as: [calcd from (11)] − [observed].

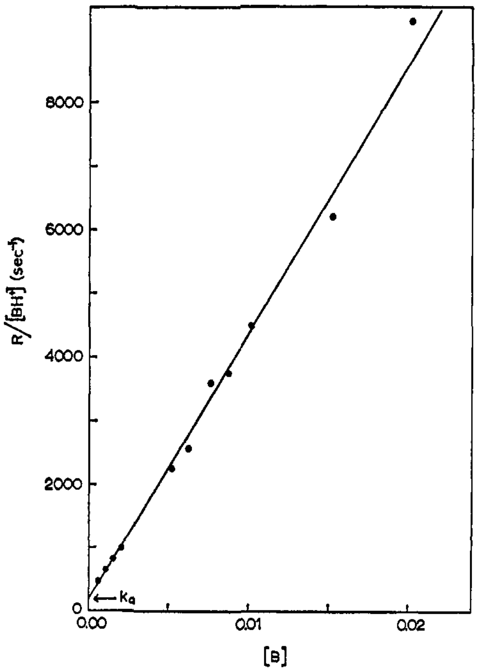


Figure 4. Proton-exchange kinetics of BH^+ in methanol at pH >4.7. Under those conditions, eq 11 reduces to $R/[BH^+] = k_a + k_2[B]$. The straight line is drawn according to the rate constants listed in Table I.

again random. It should be noted that between pH 3.5 and 5.0 the control of the pH in the nmr sample tubes is especially difficult because of the poor buffering action in that pH range. All facts considered, we believe that the small, apparently systematic, deviations between pH 3.5 and 5.0 should be disregarded. Rate constants giving best fit are shown in Table I.

The kinetic term $k_2[B]$ in (11) is due to reaction 6. It was shown (Table I, footnote *b*) that one methanol molecule participates in that reaction. The magnitude of k_2 is surprisingly small. In previously reported examples,[3,6–11] the rate constant for an alkyl- or arylammonium ion undergoing reaction 6 was 10^7 sec^{-1} M^{-1} or greater.

Discussion

In this discussion, which continues that of an earlier paper,[2] we appraise the effect of nonpolar substituents on the rate constant, k_H, for the dissociation of an amine solvate. In the present work the nonpolar substituent was added onto the solvent molecule; in the earlier work it was added onto the amine molecule. In the earlier work we examined the data for a series of nonpolar amine hydrates in water and found that k_H decreases with increasing size and number of alkyl substituents. The decrease was sizable for ammonia and the methylamines, but leveled off as the nonpolar substituents became larger than C_2H_5. k_H ranged from 2.2×10^{11} for $H_3N \cdot HOH$ to 3.8×10^9 for $(C_2H_5)_3N \cdot HOH$ and 2.7×10^9 sec^{-1} for the hydrate of $(C_6H_5CH_2)_2NCH_3$.[2] The effect could be ascribed to London dispersion interaction[5] between the nonpolar groups and the departing water molecules. Semiquantitative calculation of the interaction energy gave results of the correct magnitude.[2] It was not necessary to complicate our model by assuming the formation of "structured" or "clathrate" water.[12,13]

If the London dispersion interaction is indeed dominant,[4b] then we predict analogous reductions in k_H as the hydroxylic solvent molecule changes from HOH to CH_3OH to *t*-BuOH. Inspection of Table I shows that this prediction is in agreement with observation, and that the substituent effects are strikingly large. For B·HOH and B·HOBu-*t* k_H was measured under indentical conditions, in 11.47 mole% *t*-BuOH–water, and the results are strictly comparable. For $B \cdot HOCH_3$ k_H was measured in methanol, a less viscous solvent, and that result is not strictly comparable to the others. If k_H for $B \cdot HOCH_3$ could be measured directly in *t*-BuOH–water, the value would probably be somewhat smaller.

Because the London dispersion energy is sensitive to the detailed geometry of the solvation complexes, we have constructed three-dimensional molecular models, using CPK space-filling atomic models,[14] to estimate the preferred conformations. We assumed that the N·HO hydrogen bond formed by N,N-diethyl-*m*-toluidine is nearly linear. Then, in the case of the amine hydrate, the water-hydrogen atom not involved in the hydrogen bond has no obviously preferred conformation. In the case of the methyl alcoholate, there may be a slight preference for those conformations that

---

(11) E. Grunwald and A. Y. Ku, *J. Am. Chem. Soc.*, **90**, 29 (1968).

(12) The term "structured water" has a wide spectrum of meanings. Some authors use it to suggest merely that certain water molecules are less free to move than in the normal liquid, without implying any particular mechanism of constraint or geometry of molecular packing. Others use it very specifically to denote, for example, hydrogen-bonded cage structures such as those found in crystalline clathrates or in various forms of ice.

(13) For early discussions of "clathrate water," see, for example, (a) R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951); (b) W. F. Claussen and M. F. Polglase, *ibid.*, **74**, 4817 (1952); (c) D. D. Eley, *Trans. Faraday Soc.*, **35**, 1281 (1939); (d) D. N. Glew and E. A. Moelwyn-Hughes, *Discussions Faraday Soc.*, **15**, 150 (1953).

(14) Ealing Corp., Cambridge, Mass. 02140.

bring the alcohol–methyl group closer to the benzene ring. In the case of the *t*-butyl alcoholate, however, there is one conformation in which the N·HO group is nearly linear that brings two methyl groups of the *t*-butyl group close to the benzene ring so that the van der Waals radii just touch. In that conformation, the contours of the space-filling molecular models are nicely complementary and the two molecules form a hydrogen-bonded solvation complex with almost perfect geometry of packing. Let us assume that there is a strong preference for that particular conformation. To dissociate the solvation complex, it is then necessary to overcome substantial attractive forces not only at the site of the N·HO hydrogen bond but also at the two sites where methyl groups of the *t*-butyl group are adjacent to the benzene ring. We might expect, therefore, that the activation energy for dissociation of the *t*-butyl alcoholate is relatively high and that k_H is relatively small. One is reminded, of course, of the way in which a substrate molecule is said to fit onto its specific site on the surface of an enzyme.

When we calculate the London dispersion energy, these ideas can become semiquantitative. Calculations were made for the conformations described above, using eq 15 of the previous paper[2] and numerical data (atomic and group polarizabilities, ionization energies, and bond lengths) taken from Table IV of that paper.[2] Results of the calculation are that replacement of HOH by $HOCH_3$ at the hydrogen-bonding site of N,N-diethyl-*m*-toluidine increases the magnitude of the London dispersion energy by about 1.0 kcal; replacement of HOH by HOBu-*t* increases it by about 6.7–7.9 kcal. Results of observation are that solvation by methanol rather than by water raises $-RT \ln k_H$ by 1.6 kcal; solvation by *t*-butyl alcohol rather than by water raises it by 6.0 kcal. The agreement of the semiquantitative calculation with observation is quite impressive, considering the magnitude of the effect, and is about as good as it was in the earlier work[2] on the effect of nonpolar substituents in the amine on k_H for the amine *hydrate* in water. It should be noted that, while it was necessary to consider the solvent–solute interaction in considerable detail, it was not necessary to consider the solvent–solvent interaction at all.

Because of the well-known existence of solid clathrates consisting of a hydrocarbon in a water lattice, it is sometimes thought that lattice structures of water molecules can build up next to nonpolar molecules also in liquid solution.[13,15] Such a theory emphasizes the water–water interaction and de-emphasizes the water–solute interaction, because the water molecules arrange themselves in the clathrate-like segments of the solvation shell so as to optimize their mutual hydrogen bonding. It is even thought, in extreme versions of this theory, that the clathrate-like water lattice forms a cage around the nonpolar solute molecule, as if the solute molecule were clothed in a suit of armor.

Our own view, which developed from our k_H measurements, is near the opposite end of the theoretical spectrum. Most organic molecules have complex contours with protrusions and nooks and crannies. Water molecules are small and can pack efficiently around such contours, but only if there is some deformation of their normal hydrogen-bonded structure. Our k_H measurements seem to indicate that the interaction energy to be gained by the close approach of water molecules to the solute molecule is very substantial and that the necessary deformation of the normal water structure takes place. Rather than in a suit of armor, the solute molecule is clothed in a form-fitting sweater!

Experimental Part

Materials. Commercial N,N-diethyl-*m*-toluidine was purified by careful fractionation under reduced pressure and stored under nitrogen: base equiv wt, 163.5, 164.0 (calcd, 163.3). N,N-Diethyl-*m*-toluidinium chloride was prepared from the toluidine and a slight excess of hydrochloric acid. The viscous solution was taken to dryness on a rotary evaporator, and the last traces of water were removed by azeotropic distillation with benzene. The product was recrystallized twice from benzene and the white crystals that resulted were vacuum dried, mp 138–138.5°.

N,N-Dimethyl-*p*-nitroaniline was recrystallized from ethanol to give bright yellow-orange needles, mp 162–163°. Absorbance measurements were made at 390 mμ, where ϵ 1.906×10^4 M^{-1} cm^{-1} in methanol at 26°. p$K_A{}^0$ (extrapolated to infinite dilution) of N,N-dimethyl-*p*-nitroanilinium ion is 0.05 in methanol at 26.2° and −0.84 in 11.47 mole % *t*-BuOH–88.53 mole % water at 26.7°.

Methanol, *t*-butyl alcohol, and water were purified as described previously.[6,16] Solutions of dry hydrogen chloride in methanol were prepared from pure methanol and hydrogen chloride gas that had been dried by bubbling through concentrated sulfuric acid. Solutions for kinetic experiments were prepared from the pure reagents by standard quantitative techniques.

pH Measurements. We define pH = p$_c$H = −log (concentration of H^+). Above pH 3, measurements were made with a Beckman research pH meter and a glass–Ag|AgCl "combination electrode" (Beckman No. 39030). For reaction mixtures in *t*-butyl alcohol–water, pH was measured in a small glass reservoir fused directly to the top of the nmr sample tube. The pH meter was calibrated and made direct-reading with standard 10^{-2} to 10^{-3} *M* HCl to which 0.1 or 0.2 *M* BHCl had been added. For reaction mixtures in methanol, pH was measured externally and the nmr sample tube was cleaned by thorough rinsing, first with solvent and then with the sample solution. The accuracy of pH measurements in methanol was checked with standard 10^{-2} to $10^{-3.5}$ *M* HCl to which 0.05 *M* BHCl had been added; it was found that δpH = $-\delta \log [H^+]$.

pK_A Measurements. In *t*-butyl alcohol–water, pK_A of N,N-diethyl-*m*-toluidinium ion was measured by the differential potentiometric method[17] at 25°. pK_A increased systematically from 5.35 at 0.1 *M* BHCl to 5.38 at 0.4 *M* BHCl. In methanol, pK_A was measured at 30° by the nmr kinetic method described previously.[18] pK_A was also measured potentiometrically at 22°. Results are listed in Table I.

Nmr Measurements. T_2 and T_1 for the OH-proton resonance or exchange-averaged OH–NH proton resonance was measured by Alexander's method[19] to minimize interference beats from the methyl protons. In the absence of exchange broadening, T_1/T_2 was 1.07 ± 0.01 in both solvents. Exchange broadening was therefore taken to be $(1/T_2) - (1.07/T_1)$.

The rate of NH–OH proton exchange was calculated from the exchange broadening, using equations given previously.[20] The following values were used for the required nmr parameters. In *t*-butyl alcohol–water at 25°, $\delta_{NH-OH} = 2138 - 164[HCl]$ sec^{-1} (where [HCl] denotes the molar concentration); T^1 of ^{14}N = 0.7 msec and J_{NH} = 314 sec^{-1}. The last two values are plausible estimates. In methanol at 30°, δ_{NH-OH} = 1618 sec^{-1}; T^1 of ^{14}N = 1.9 msec (estimated), and J_{NH} = 314 sec^{-1} (estimated).

---

(15) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945); H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(16) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem Soc.*, **84**, 4664 (1962).

(17) A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(18) E. Grunwald and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 2047 (1963).

(19) S. Alexander, *Rev. Sci. Instr.*, **32**, 1066 (1961).

(20) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2965, 2970 (1964).

In methanol there was additional exchange broadening of the OH resonance due to incomplete averaging of that resonance by hydrogen ion catalyzed OH-proton exchange. This additional exchange broadening is the sum of two terms, $B_Q + B_{O\text{-}17}$, owing to (B_Q) transfers between the individual components of the OH spin-spin quadruplet, and ($B_{O\text{-}17}$) transfers between $CH_3{}^{16}OH$ and CH_3-^{17}OH at natural isotopic abundance. The theory has been stated by Grunwald, Jumper, and Meiboom.[21] $B_{O\text{-}17}$ was calculated according to eq 4 of that paper, using $\tau_1 = 2.80 \times 10^{-10}/[H^+]$ at 30° and J' and T^1 of ^{17}O as given in that paper.[21] B_Q at 30° was calculated from (12), which can be obtained from eq 2 of that paper.[21]

$$B_Q = (2.19 \times 10^{-7}[H^+])(2 + 2.50 \times 10^{-14}[H^+]^2)/(1 + 2.50 \times 10^{-14}[H^+]^2) \quad (12)$$

The exchange broadening, $B_{NH\text{-}OH}$, due to NH-OH proton exchange was taken as the difference (13).

$$B_{NH\text{-}OH} = (1/T_2) - (1.07/T_1) - B_Q - B_{O\text{-}17} \quad (13)$$

In methanol also, some solutions that exhibited a large amount of exchange broadening were examined in slow passage (rather than by spin-echo) and gave kinetic results in agreement with those obtained by direct measurement of T_2 and T_1.

Acidity Function for Tertiary Anilines in *t*-BuOH-HOH-HCl. In order to interpret kinetic data at high HCl concentrations, we measured the Hammett acidity function H_0,[22] using N,N-dimethyl-*p*-nitroaniline (I) as indicator. $pK_A{}^0$ for IH^+ was found to be −0.84 at 26.7° in 11.47 mole % *t*-BuOH-88.53 mole % water. In preparing the concentrated solutions, the alcohol/water mole ratio was kept constant as HCl was added. By definition, $H_0 = pK_A{}^0 + \log (I)/(IH^+)$. (I) was measured spectrophotometrically at 26.7° and 390 mμ. Between 0.20 and 3.25 *M* HCl, H_0 was an accurately linear function of pH and [HCl], according to

$$H_0 = p_cH - (0.493 \pm 0.005)[HCl] \quad (14)$$

By using H_0 rather than pH for the measure of acidity, we were able to extend our kinetic analysis to rather high HCl concentrations.[2,9] It was found that the viscosity of these solutions increases by no more than a few per cent in the experimental range, and changes in viscosity were therefore neglected. The theoretical curve in Figure 2 is calculated using h_0 instead of $[H^+]$, where $-\log h_0 = H_0$. The fit of the data is good up to the highest HCl concentration, 2.6 *M*.

In treating the data in methanol, it was not considered necessary to use an acidity function rather than p_cH because the rate became too slow to be measurable accurately at about 0.6 *M* HCl.

---

[21] E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).

[22] See, for example, E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964), and references cited therein.

Conversion of Electronic Excitation into Thermal Energy. Effect of Solvent and Substituents in the 4 and 5 Positions on Absorption and Fluorescence Spectra of 1,3-Diphenyl-Δ^2-pyrazolines

Zbigniew Raciszewski and J. F. Stephen

Contribution from the Research and Development Department,
Union Carbide Corporation, Chemicals and Plastics,
South Charleston, West Virginia 25303. *Received December 31, 1968*

Abstract: Investigated were 1,3-diphenyl-Δ^2-pyrazoline (**4**), compounds obtained by fusion of **4** to the cyclopentane (**5**) and the norbornane (**6**) rings, and derivatives of **5** and **6** with substituents in the 5-pyrazoline position. From the absorption and fluorescence spectra recorded in cyclohexane and isopropyl alcohol, and the photostability tests, were calculated the quantum yields of fluorescence (Φ_f) and of photodegradation (Φ_d), the ratio of quanta converted into thermal energy to quanta emitted as light (Θ), and the lifetimes of the excited states: actual (τ), radiative (τ_0), and nonradiative (τ_{nr}). Isopropyl alcohol produced a *blue* shift in the absorption spectra (except for the hydroxy derivative of **6**) and a *red* shift in the fluorescence spectra indicating stabilization, relative to cyclohexane, of the ground state and, after relaxation of the solvent cage had occurred, of the excited state. Fusion of **4** to the cyclopentane or norbornane resulted in *red* shifts in the absorption spectra, but the shifts were obliterated by the second substituent in the 5 position. The Φ_d figures did not exceed 0.00025 and the Φ_f's ranged from 0.52 to 0.94. Efficiency in the conversion of electronic excitation into thermal energy, measured by Θ, was governed by the rigidity of the molecule and the solvent; least efficient was **6**. Isopropyl alcohol markedly increased this efficiency in **4** but had no effect on **6**. Substitution of **6** increased the Θ; the hydroxyl and the dimethylpiperazinium groups were most effective. Rates of fluorescence, $1/\tau_0$, were slightly retarded by isopropyl alcohol and little affected by structural modifications, except for the hydroxy derivative of **6** in cyclohexane. Consequently, differences in the efficiency in the conversion of electronic excitation into thermal energy were principally manifested in changes in the nonradiative lifetimes, τ_{nr}.

Fluorescence of 1,3-diphenyl-Δ^2-pyrazolines has been attributed to planarity of the molecule and the presence of two substituents, capable of interaction by way of the mesomeric forms **1b** and **1c**.[1-6] The nonplanar compounds **2** and **3** do not fluoresce,[1,4] and marked changes in the emission of light are induced by

---

[1] O. Neunhoeffer and D. Rosahl, *Z. Elektrochem.*, **57**, 81 (1953).

[2] O. Neunhoeffer and H. Ulrich, *Ber.*, **88**, 1123 (1955).

[3] O. Neunhoeffer, G. Alsdorf, and H. Ulrich, *ibid.*, **92**, 252 (1959).

[4] A. Wagner, C. W. Schellhammer, and S. Petersen, *Angew. Chem., Intern. Ed. Engl.*, **5**, 699 (1966).

[5] A structure alternative to **1b** and **1c**, with the partial positive charge localized on the C-3 of the pyrazoline ring, has been suggested in ref 6.

[6] S. R. Sandler and K. C. Tsou, *J. Chem. Phys.*, **39**, 1062 (1963).